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VARIATIONS IN HOMOGENEOUS FLUORESCENCE LINEWIDTH

AND ELECTRON-PHONON COUPLING WITHIN AN INHOMOGENEOUS SPECTRAL PROFILE


by

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In this communication we use the fluorescence line narrowing technique (FLN) to determine the homogeneous width of the $^5D_o \rightarrow \, ^7D_o$ resonance fluorescence line of $Eu^{3+}$ in an amorphous silicate matrix as a function of laser excitation wavelength and temperature (200-350°K). A smooth increase in $\Delta\nu_{hom}$ is observed as the excitation wavelength is decreased across the inhomogeneous profile (excitation of sites of progressively higher average crystal field. The combined temperature and excitation wavelength dependence

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identify the broadening mechanism as a two-phonon Raman scattering process and suggest that the observed increase of $\Delta\nu_{hom}$ with increasing excitation energy is due to stronger electron-phonon coupling at sites of stronger crystal field.

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# VARIATIONS IN HOMOGENEOUS FLUORESCENCE LINEWIDTH AND ELECTRON-PHONON

## COUPLING WITHIN AN INHOMOGENEOUS SPECTRAL PROFILE

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The origin of the homogeneous optical linewidth in ionic and molecular solids is a subject of considerable current interest. In most systems at finite temperatures the homogeneous width ($\Delta\nu_{hom}$), or in an equivalent description the optical transverse relaxation time ($T_2$),[1] is determined by phase destructive events. The measurements of homogeneous broadening are performed either in the frequency domain[2-9] or in the real time domain.[10-12]

In this communication we use the fluorescence line narrowing technique[2] (FLN) to determine the homogeneous width of the $^5D_0 \rightarrow {}^7F_0$ resonance fluorescence line of $Eu^{3+}$ in an amorphous silicate matrix as a function of laser excitation wavelength and temperature (200-350°K). A smooth increase in $\Delta\nu_{hom}$ is observed as the excitation wavelength is decreased across the inhomogeneous profile (excitation of sites of progressively higher average crystal field[13]). The combined temperature and excitation wavelength dependence identify the broadening mechanism as a two-phonon Raman scattering process and suggest that the observed increase of $\Delta\nu_{hom}$ with increasing excitation energy is due to stronger electron-phonon coupling at sites of stronger crystal field.

$Eu^{3+}$ 0.09 mole % was incorporated as an impurity in a sodium barium zinc silicate matrix. The experimental setup has been described earlier.[14] Upon exciting with a narrow laser line ($\sim 1$ cm$^{-1}$), an emission in resonance with, but broader than, the laser line is observed. In addition, a weak broad

side band appears whose intensity and position vary with the excitation wavelength and the temperature. Further studies of these side bands are now in progress and will be published later. The resonant fluorescence lineshape is Lorentzian to a very good approximation.

The important results are shown in Figs. 1 and 2 and can be summarized as follows: (i) Fig. 1 shows a smooth increase in the homogeneous fluorescence linewidth (corrected for the finite laser and instrumental widths) as the excitation wavelength of the laser is decreased across the inhomogeneous line ($\Delta\nu_{hom}$ changes by a factor of 2 between 5795 and 5745 Å). (ii) The variation of $\Delta\nu_{hom}$ with temperature can be fitted to a power law, $T^n$, with $n = 2.1 \pm 0.1$ (Fig. 2) or to an exponential law, $e^{-\Delta E/kT}$, with an activation energy $\Delta E = 380 \pm 20$ cm$^{-1}$, and is independent of the excitation wavelength.

From $\Delta\nu_{hom}$, $T_2$ can be obtained from the relation $T_2^{-1} = \pi\Delta\nu_{hom} = (2T_1)^{-1} + \Gamma \simeq \Gamma$, where $T_1$ is the longitudinal relaxation time, which in our case is determined essentially by the radiative lifetime ($\sim 1$ ms), and $\Gamma$ is the dephasing rate. From Fig. 1, $T_2$ is found to change from 1.5 to 4 psec across the inhomogeneous band and is determined by the loss of phase coherence as a result of one- or two-phonon scattering processes. The variation of $\Delta\nu_{hom}$ (or $T_2$) across the inhomogeneous profile then signifies a variable efficiency of the phonon scattering processes with excitation wavelength.

The variation in $\Delta\nu_{hom}$ with $\lambda_{exc.}$ and temperature could be explained by either a Raman process (since a one-phonon process is expected to show a linear temperature dependence[15]),with a site-dependent electron-phonon coupling strength, or by an Orbach process with a site-dependent activation energy. The linewidth decreases with increasing $\lambda_{exc.}$ (indicating a smaller scattering rate) so that the Orbach activation energy would have to increase to explain our observation. The only accessible ion level whose transition energy changes in this direction is the lowest Stark component

of the $^7F_1$ level, which lies from 130-260 cm$^{-1}$ above the ground state. The observed activation energy is 380 ± 20 cm$^{-1}$ and, more important, is independent of $\lambda_{exc}$. Thus we conclude that the Orbach mechanism is unimportant in this system.

A Raman process should exhibit a $T^7$ dependence for $T < T_{Debye}$ or $T^2$ for $T \gtrsim T_{Debye}$.[15] Since a power law fit of our data gives $T^{2.1\pm0.1}$ over a temperature range where $T \gtrsim T_{Debye}$ (200-350 K), a Raman process is indicated. The variation in the homogeneous linewidth across the inhomogeneous profile is then ascribed to a site-dependent electron-phonon coupling strength.

Brecher and Riseberg[13] showed that, in this silicate glass, high $^5D_0 \rightarrow {}^7F_0$ excitation energies of Eu$^{3+}$ correspond to high static crystal fields. As our results suggest, high excitation energies also correspond to stronger electron-phonon coupling. Therefore, there appears to be a correlation between the crystal field and electron-phonon coupling strengths. This correlation is physically reasonable since the electron-phonon coupling measures the modulation of the crystal field by the thermal lattice strains. The $^7F_0$ and $^5D_0$ levels may be affected by the electron-phonon perturbation to different extents. We suggest that phonon perturbation of the ground state is dominant in determining the observed homogeneous linewidth. This is based on the following simplified argument. The interaction Hamiltonian consists of a linear electron-phonon coupling term taken to second order and a quadratic term taken to first order. If the linear term dominates, and if the matrix elements are similar for the $^7F_0$ and $^5D_0$ levels, then the relative amount of broadening is determined by the sizes of the energy denominators in the perturbation expansion. Furthermore, the major contribution to the sum over levels will come from mixing of J = 0 with J = 2 levels.[16,17] Since $\Delta E(^5D_0 - {}^5D_2)$ is ~ 2.5 $\Delta E(^7F_0 - {}^7F_2)$,[18] perturbation of the ground state is expected to be dominant.

In closing, we conclude that: (i) variations of the phonon scattering efficiency and transverse relaxation rate may appear within a single inhomogeneously broadened line, (ii) correlations between the scattering efficiency and static crystal field may exist, and (iii) the measurement of phase destructive events in the frequency domain is a powerful and simple technique for studying events on the picosecond time scale.

## ACKNOWLEDGMENTS

## References

1. L. Allen and J. H. Eberly, Optical Resonance and Two-Level Atoms, Wiley-Interscience, N.Y., 1975.

2. A. Szabo, Phys. Rev. 25, 924 (1970).

3. A. Szabo, Phys. Rev. B11, 4512 (1975).

4. T. Kushida and E. Takushi, Phys. Rev. B12, 824 (1975).

5. P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen and M. J. Weber, Phys. Rev. Lett. 36, 813 (1976).

6. M. J. Weber, J. A. Paisner, S. S. Sussman, W. M. Yen, L. A. Riseberg and C. Brecher, J. Lumin. 12/13, 729 (1976).

7. B. M. Kharlamov, R. I. Personov and L. A. Bykovskaya, Opt. Comm. 12, 191 (1974).

8. A. P. Marchetti, W. C. McColgin and J. H. Eberly, Phys. Rev. Lett. 35, 387 (1975).

9. H. de Vries and D. A. Wiersma, Phys. Rev. Lett. 36, 91 (1976).

10. A. Z. Genack, R. M. Macfarlane and R. G. Brewer, Phys. Rev. Lett. 37, 1078 (1976).

11. T. J. Aartsma, D. A. Wiersma, Phys. Rev. Lett. 36, 1360 (1976).

12. A. H. Zewail, T. E. Orlowski and R. D. Dawson, Chem. Phys. Lett. 44, 379 (1976).

13. C. Brecher and L. A. Riseberg, Phys. Rev. B13, 81 (1976).

14. P. Avouris, A. Campion and M. A. El-Sayed, Phonon Assisted Site-to-Site Electronic Energy Transfer Between $Eu^{3+}$ Ions in an Amorphous Solid, Chem. Phys. Lett., in press.

15. B. DiBartolo, "Optical Interactions in Solids," J. Wiley & Sons, N.Y., 1968.

16. R. Orbach, Phys. Rev. 133, 34 (1964).

17. N. Motegi and S. Shionoya, J. Lumin. 8, 1 (1973).

18. R. Reisfeld, J. Res. N.B.S. 76A, 613 (1972).

## Figure Captions

Fig. 1    The variation of the homogeneous linewidth of the $^5D_0 \rightarrow {}^7F_0$ resonance fluorescence line of $Eu^{3+}$, in a silicate glass at 393 K, with laser excitation wavelength within the inhomogeneous line profile. Also indicated is the optical transverse relaxation rate $(T_2^{-1})$ under the same conditions.

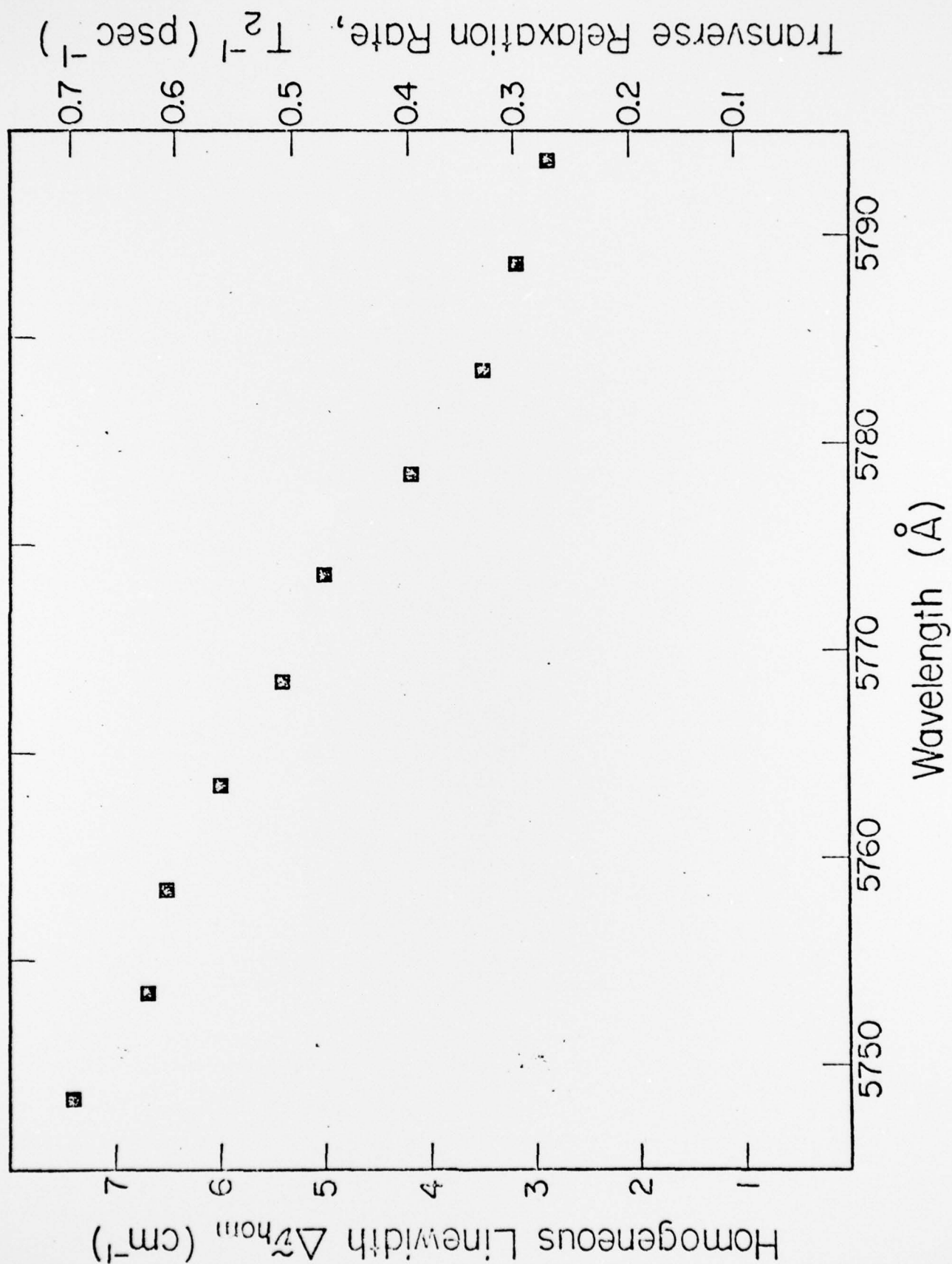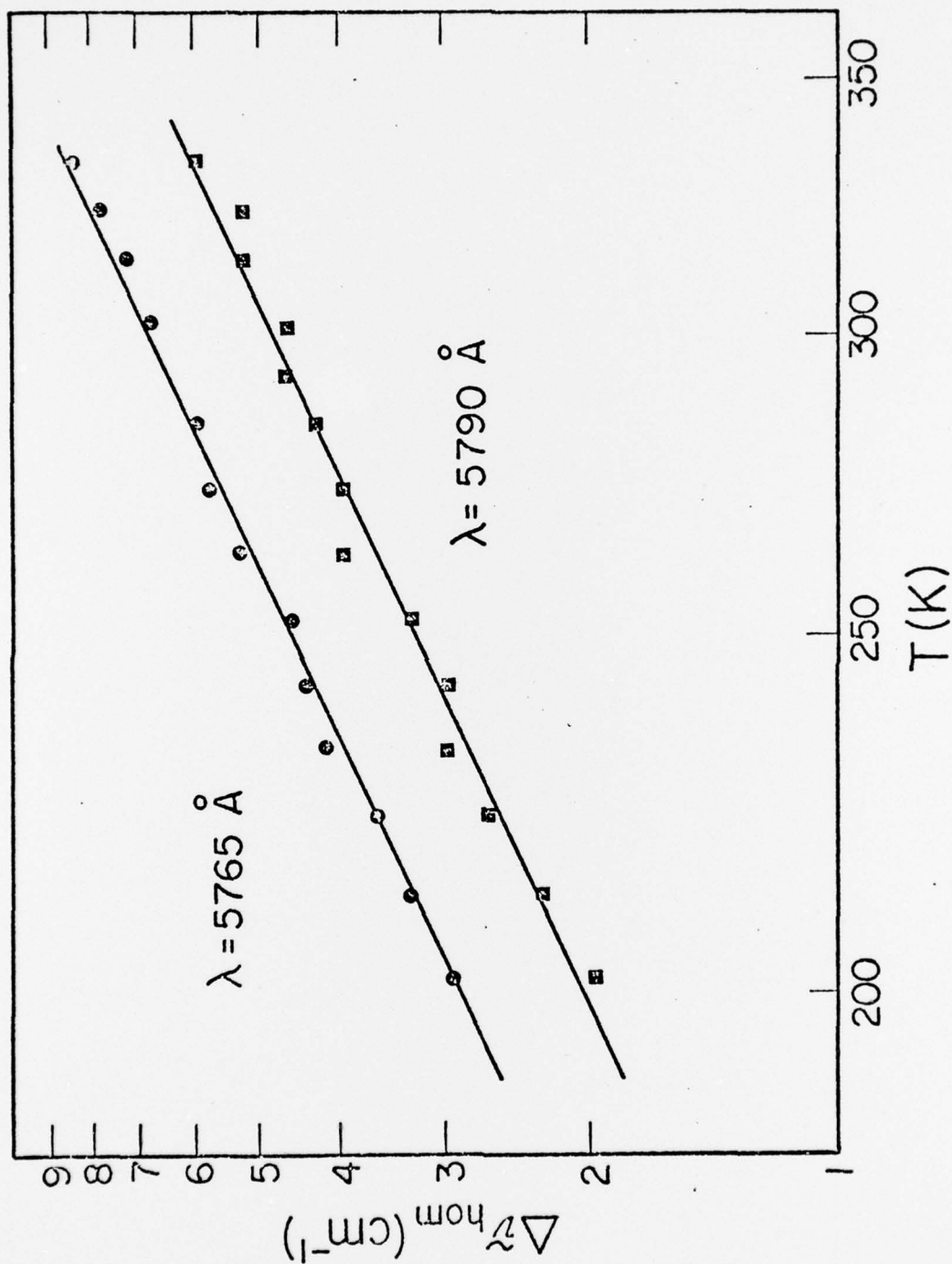Fig. 2    The dependence of the homogeneous linewidth on temperature.

Figure 1

Fig 1

Figure 2.

$\lambda = 5765$ Å

$\lambda = 5790$ Å

T (K)

$\Delta \tilde{\nu}_{hom}$ (cm$^{-1}$)

Fig 2

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